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COMPLETE SPECIFICATION

Graft Copolymers and process for preparing them

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, a body corporate recognised under German law, of (16), Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to graft copolymers and to a process for their preparation.

A graft polymer is a highly polymeric substance, the molecules of which are composed of two or more polymeric portions of different composition which are linked by main valences. A graft copolymer can be produced, for example, by performing the polymerization of a monomer in the presence of a preferred polymer. According to the nature of the polymer used the grafting can take place at the ends of the polymer chains or along said chains by means of known chain transfer mechanisms.

As compared with the usual copolymers the corresponding graft copolymers have quite different physical properties, as a result of which new and interesting fields of application have already opened up for the graft copolymers.

Particularly interesting are graft copolymers of polyvinyl esters with polyalkylene-oxides or-glycols or derivatives thereof.

It has been proposed to manufacture graft copolymers with polyalkylene oxides by grafting monomeric alkylene oxides on to polymers having reactive groups.

It has also been proposed, for example, to produce graft copolymers by the action of ethylene oxide on polymers containing active hydrogen, such as cellulose and polyamides.

U.S. Patent No. 2,602,079 describes a two-stage process for the manufacture of oxyalkylated polymers of vinyl esters. In the first stage, for example, a higher vinyl ester, such as vinyl palmitate or vinyl laurate is polymerized in xylene with dibenzoyl peroxide and

in the second stage the polymer is then oxethylated in an autoclave, after the addition of sodium methylate, by introducing ethylene oxide at 160°C and under a pressure of 10 atmospheres.

This process is complicated and dangerous and, moreover, not very economical owing to the use of solvents.

The present invention is based on the observation that graft copolymers of polymerizable compounds, preferably vinyl esters and esters of acrylic or methacrylic acid, can be produced in a surprisingly simple manner on polyalkylene oxides or polyalkylene glycols or suitable derivatives of such compounds (referred to hereinafter in the interests of brevity also as polyalkylene glycols) by dissolving the polyalkylene glycol in at least one monomer in the presence or absence of additional solvents, and by polymerizing the monomer or monomers in homogeneous phase in the presence of a free radical polymerisation catalyst and/or under the action of actinic light.

Polyalkylene glycols are readily soluble in the aforesaid monomers. When they are used more than 10% by weight of polyalkylene glycol, calculated on the monomer, it may be of advantage to heat the batch slightly to 30—40°C in order to accelerate the dissolution. Said solutions can then be polymerized under known conditions. It may be advisable to start the polymerization in a part of the solution by heating and to add the residual solution after the beginning of the reaction.

It is likewise possible to operate in a manner such that the polyalkylene glycol is introduced into the polymerization vessel separately from the monomer and that the polyalkylene glycol is first dissolved in the monomer in the reaction vessel. It is, furthermore, possible to charge the polymerization vessel first with the whole amount of polyalkylene glycol, for example polyethylene glycol, and then to add the monomer, preferably at elevated temperature, for example at about 70°C.

In general it is of advantage to carry out

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the polymerization in the presence of inert gases, for example nitrogen.

The polymerization may, of course, also be carried out in a continuous manner.

- 5 Transparent or slightly translucent graft copolymers are obtained containing 30 — 100% by weight of the polyalkylene glycol used bound to the grafted polymer. The unreacted polyalkylene glycol can be separated
 10 from the graft polymer, for example, by repeatedly dissolving and reprecipitating the polymer. For many industrial applications it is possible, however, to use the crude product as obtained in the polymerization so that in
 15 these cases a purification can be dispensed with.

The chemical analysis of the novel products indicates that the grafting of the monomers along the polyalkylene glycol chains is induced by means of a radical-forming chain transfer mechanism. To improve the probability of transfer, it is preferred to polymerize in homogeneous phase in the absence of additional solvents.

- 20 25 The properties of the graft copolymers produced by the process of the invention differ substantially from the properties of pure mixtures of polymers, for example, mixtures of a polyvinyl ester with a polyalkylene glycol, for example; as regards the behaviour of
 30 methanolic solutions upon precipitating with water.

As monomers that can be used in the process of the invention there may be mentioned
 35 by way of example vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate, esters of acrylic or methacrylic acid with lower aliphatic alcohols having 1—8 carbon atoms, such as methanol, ethanol, n- or iso-propanol,
 40 the various isomeric butanols and ethylhexanol. The aforesaid monomers can be used in the graft polymerization either alone or in admixture with one another or with other copolymerizable compounds, such as crotonic acid, acrylic or methacrylic acid, maleic acid or fumaric acid esters, for example, maleic acid dimethyl ester, fumaric acid dibutyl ester or itaconic acid dibutyl ester.

- 45 50 As free radical polymerization catalysts there may be used the usual types, preferably those that are soluble and form radicals in organic media, for example diacetyl peroxide, dibenzoyl peroxide, dilauroyl peroxide or, z:z - azodiisobutyronitrile, in an amount ranging from 0.01 to about 10% and preferably 0.1 to 2%, calculated on the weight of the monomer or monomers used. An activation by means of redox catalysts is likewise possible, for example, with the system dibenzoyl peroxide/benzoin and/or by irradiation, especially with actinic light.

55 60 The reaction temperature depends on the monomer used and on the catalyst system. In general the reaction is carried out at a temperature in the range from 50 to 100°C.
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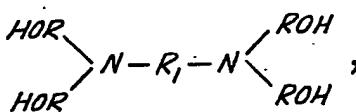
When suitable redox systems are used, it is also possible to operate at lower temperatures, and if desired, at higher temperatures, possibly under pressure.

70 As polyalkylene glycols there are suitable, for example, polyethylene glycols having a molecular weight of 106 to several millions, preferably in the range from 1,000 to 30,000, furthermore, polypropylene glycols and polymers of higher alkylene oxides. There may also be used products composed of co- and terpolymers of ethylene oxide, for example with propylene oxide, 1:2 - epoxy - butane, isobutylene oxide, and compounds of the aromatic series, such as styrene oxide.

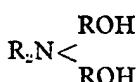
75 80 From among the copolymers composed, for example, of ethylene oxide and propylene oxide, there are suitable the copolymers containing the comonomers in statistical distribution as well as copolymers with alternating larger polypropylene glycol segments and polyethylene glycol segments. In the latter case a novel class of compounds is obtained which are "branch" as well as "block" graft copolymers when vinyl and acrylic esters are reacted. As regards the definitions "block graft copolymers" and "branch graft copolymers" reference is made, for example, to H. Mark, Ang. Chemie, 65, pages 53—56 (1955), and H. Mark, Textile Res. Journ. 23, page 294 (1953). It is to be understood that the term "graft copolymers" is used herein to include both branch and block graft copolymers.

85 90 95 Especially interesting are oxyethylated polypropylene glycols which consist, for example, of a central portion of polypropylene glycol having a molecular weight of about 2,000 to 12,000, and which are reacted at both ends with about 40 to 70 mols of ethylene oxide. High proportions of said products can be used, for example, in the graft polymerization with vinyl esters.

100 105 110 115 120 125 As suitable derivatives of polyalkylene glycols in the process of the invention there may be mentioned polyalkylene glycols the terminal hydroxyl groups of which are etherified or esterified at both ends or at one end only with mono- or poly-functional compounds, for example, etherified with methanol or butanol or esterified with acetic acid, propionic acid or butyric acid, and which are known, inter alia, as non-ionic emulsifiers. Furthermore, nitrogen-containing polyalkylene glycols can be used, such as 1) compounds the terminal hydroxyl groups of which are substituted at both ends or at one end only of the chain by mono- or polyfunctional amines, for example compounds of the type



wherein R stands for an alkylene oxide chain having 3 to more than 2,000 units, which chain may consist of a uniform alkylene oxide, for example ethylene oxide, propylene oxide or the higher homologues thereof or of copolymers of different alkylene oxides either in statistic distribution or in the arrangement of alternating blocks, R₁ represents a hydrocarbon radical, such as alkylene, arylene or a corresponding mixed aromatic - aliphatic radical,
 5 2) compounds the terminal hydroxyl groups of which are substituted at both ends or at one end only of the chain by mono- or poly-
 10 15 functional carboxylic or sulphonic acid amides, for example, compounds of the type



wherein R has the meaning given above and R₂ stands for a carboxylic or organic sulphonate acid radical, for example, the group
 20 CH₃CO— or C₆H₅—SO₃—.

The nitrogen - containing polyalkylene glycols defined under 1) and 2) above may likewise have a constitution such that the
 25 two terminal hydroxyl groups of the poly-

alkylene glycol portion carry two different substituents of the aforesaid nature or only one nitrogen-containing radical and one of the ether or carboxylic acid radicals already mentioned.

In the case of polyfunctional nitrogen-containing substituents, for example diamines, such as ethylene diamine, propylene diamine, butylene diamine and hexamethylene diamine or in the case of dicarboxylic acid amides several or all of the hydrogen atoms capable of being substituted can be replaced by polyalkylene glycol radicals which are identical or different with respect to the nature of the polyalkylene glycol as well as to the degree of polymerization thereof.

The molecular weight of the aforesaid nitrogen-containing polyalkylene glycols varies between about 500 and several millions and preferably between about 100 and about 30,000.

The K value (according to Fikentscher, Cellulosechemie volume 13, page 58, 1932) of the graft polymers obtained with the aid of vinyl esters is lower than that of pure polymers of vinyl esters produced under identical conditions and depends on the molecular weight of the polyalkylene glycol used as shown in the following table.

Parts by weight of vinyl acetate	Parts by weight of polyalkylene glycol	molecular weight of polyalkylene glycol	Parts by weight of activator (dibenzoyl peroxide)	K value, 1% in ethyl-acetate
90	10 polyethylene glycol	25,000	1	56
90	10 polyethylene glycol	15,000	1	44
90	10 polyethylene glycol	4,000	1	40
98	2 polyethylene glycol	4,000	1	44
90	10 polyethylene glycol	400	1	36
90	10 triethylene glycol	132	1	32
98	1 oxyethylated polypropylene glycol	4,500	1	51
98	1 polypropylene glycol	2,000	1	46
99	—	—	1	55—60
90	—	—	1	55

By the process of the invention modified polyvinyl esters are obtained which, according to the nature and amount of the chemically incorporated polyalkylene glycols or the derivatives thereof, exhibit various new proper-

ties that are very interesting from an industrial point of view:

a) Modified polyvinyl esters with reduced K values are obtained, as already shown in the above table. In industrial block polymerization

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- processes of vinyl esters the K value has hitherto been reduced by regulators, chiefly aldehydes, such as propionic aldehyde or butyraldehyde.
- 5 When products of this kind are used as raw material, for example for chewing gum, a very careful purification is necessary in order to remove the last traces of aldehydes since the latter cause a disagreeable odour even if they are present in a very small amount. Such a purification, for example by means of a steam distillation, is, however, a rather complicated and expensive technical problem owing to the resinous consistency of the said block polymers. When, however, polyethylene glycols are used to reduce the K value, preferably polyethylene glycols having a molecular weight of 4000 and less, the complicated purification of the products can be dispensed with, moreover, since polyethylene glycols are physiologically harmless.
- 10 b) In the graft polymerization of vinyl acetate, for example in the presence of polyethylene glycols, preferably having a molecular weight of 15,000 and more, internally plasticized polyvinyl acetates are obtained. It is known that a film made of polyvinyl acetate is very brittle and must be rendered more flexible for many industrial applications by the addition of plasticizers, such as dibutyl phthalate. Many plasticizers are not harmless from the physiological point of view and, moreover, the use thereof involves the known danger of plasticizer migration. This disadvantage is avoided
- 15 by the incorporation of polyethylene glycols and similar compounds.
- 20 c) By the incorporation of larger amounts, for example of 50% of oxyethylated polypropylene glycol into the polyvinyl acetate, products are obtained which yield colloidal solutions in water and which are well suitable as emulsifying or dispersing agents in the
- 25 dispersion polymerization of vinyl esters. By the close relationship of the emulsifier molecule with the dispersoid of such a polyvinyl ester dispersion the film formation, which is essential for the application of dispersions of this kind, is improved in excellent manner.
- 30 d) The novel graft copolymers are furthermore very interesting for the textile industries, for example, as sizing or finishing agents or as antistatics. Furthermore, they can be used as adhesives and bonding agents in leather dressing, as basic substances for the lacquer industries, as gelatin substitute in the photographic industries or as hair treating agents.
- 35 The following examples illustrate the invention, the parts being by weight unless otherwise stated:
- 40 EXAMPLE 1
- A glass bottle provided with reflux condenser and dropping funnel is charged with 5—10 parts of a solution of
- 45 90 parts of vinyl propionate
- 50 10 parts of polyethylene glycol (mol weight about 4000)
- 55 1 part of dibenzoyl peroxide,
- 60 and polymerization started by heating the solution on a water bath at 80°C.
- 65 After the beginning of the polymerization the residual solution is dropped in over a period of about 2 hours. To complete the polymerization the bath temperature is raised to 90°C. for 1—2 hours after the addition of the polymerization mixture, whereupon the reflux ceases. The unreacted monomer is then removed at that temperature under a pulsating vacuum.
- 70 After cooling, the glass bottle with the polymer is frozen in dry ice, the bottle is smashed and the product isolated and comminuted. A very soft and sticky graft copolymer is obtained.
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- 85 EXAMPLE 2
- 90 A suitable glass bottle with a wide neck provided with a perforated cork, reflux condenser and dropping funnel is charged with 5 parts of a solution of
- 95 90 parts of vinyl benzoate
- 100 10 parts of polyethylene glycol (mol weight about 2,500)
- 100 1 part of dibenzoyl peroxide.

Analytical data	Graft copolymer	Comparative polyvinyl propionate
K value (Fikentscher)	47	—
% of carbon	59.1	60.0
% of hydrogen	8.2	8.0
% of propionyl	51.2	57.0
% of oxyethyl (Morgan)	5.8	—

The solution is heated in a water bath at 80°C until reflux and polymerization set in. The polymerization having started, further 95 parts of the above solution are added in the course of about 2 hours.

Soon after the addition of the monomer the reflux is terminated. The bath temperature is raised to 90°C and the bath maintained at this temperature for 2 hours until the poly-

merization is complete. The unreacted monomer is then removed under a pulsating vacuum.

After cooling, the glass bottle with the 5 polymer is frozen in dry ice, the bottle is

smashed and the polymer is isolated.

The comminuted insoluble graft copolymer is extracted with warm water for 4 hours and the extracted product is then dried at 40°C under reduced pressure.

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Analytical data	Graft copolymer	Comparative polyvinyl benzoate
% of carbon	69.2	73.0
% of hydrogen	5.7	5.4
% of oxyethyl (Morgan)	11.0	—

EXAMPLE 3

A solution of
15 90 parts of vinyl acetate
10 parts of oxethylated nonyl phenol
(molecular weight about 1,540)
1 part of dibenzoyl peroxide

is block polymerized as described in Example 2.

The graft copolymer is worked up in the 20 usual manner by dissolving the copolymer in methanol and reprecipitating it thrice in water, and by a subsequent drying at 40°C under reduced pressure.

Analytical data:	Graft copolymer	Comparative polyvinyl acetate
K value (Fikentscher)	38	—
% of carbon	55.6	56.2
% of hydrogen	6.9	7.0
% of acetyl	47.0	50.0
% of oxyethyl (Morgan)	3.1	—

EXAMPLE 4

A solution of
30 90 parts of vinyl acetate
10 parts of polyethylene glycol (Mol. weight about 4,000)
1 part of dilauroyl peroxide.

is block polymerized as described in Example 2.

The product obtained is worked up as usual by dissolving the copolymer in methanol and reprecipitating it thrice in water and by a subsequent drying at 40°C under reduced pressure.

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Analytical data:	Graft copolymer	Comparative polyvinyl acetate
K value (Fikentscher)	51	—
% of carbon	54.5	56.2
% of hydrogen	7.0	7.0
% of acetyl	47.0	50.0

EXAMPLE 5

In a glass bottle a graft copolymer is produced at 80°C in usual manner from a solution of

- 5 90 parts of vinyl acetate
- 1 part of benzoyl peroxide
- 5 parts of tributyl phenol condensed with
 20 mols of propylene oxide.
- 10 After the copolymer has been worked up as
 usual, 95 parts of a clear polymerization product
 are obtained having a K value of 44.2. The product
 is dissolved in benzene and precipitated in heptane and then dried at 40°C
 under reduced pressure until the weight remains constant. The polymer has an acetyl
 value of 47.8 or 47.4% as compared with 50% for pure polyvinyl acetate.

EXAMPLE 6

A four-necked flask (capacity 1 litre) provided with ground-in stirrer, dropping funnel, reflux condenser and thermometer, is charged with a mixture of

- 20 250 parts of methyl acetate
- 195 parts of vinyl acetate
- 25 50 parts of oxyethylated polypropylene glycol (mol. weight about 6,800, OH number 16.5)
- 5 parts of diacetyl peroxide in dimethyl phthalate (of about 28% strength)
- 30 The mixture is then heated under reflux and boiled for 6 hours. The dry content amounts to 45% after 3 hours and to 48% after 6 hours.
- 35 After 6 hours the mixture is allowed to cool and the copolymer is precipitated in water, dried for 100 hours at 40°C under reduced pressure and is then repeatedly dissolved in methyl acetate and reprecipitated in water. The copolymer thus purified is dried in a vacuum drier until the weight remains constant. The acetyl value amounts to 43.0% as compared with 50% for pure polyvinyl acetate.

EXAMPLE 7

45 A graft copolymer is prepared as described in Example 2 from

- 400 parts of vinyl acetate
- 32 parts of crotonic acid
- 50 40 parts of polyethylene glycol (molecular weight 4,000)
- 10 parts of dibenzoyl peroxide
- 2 parts of acetaldehyde
- 55 The clear graft copolymer obtained has a K value of 27. A corresponding copolymer produced without polyethylene glycol has a K value of 30.
- 60 In addition to its solubility in the usual polyvinyl acetate solvents the graft copolymer is distinguished by its solubility in aqueous ammonia solution.

EXAMPLE 8

An apparatus as described in Example 6 is charged with

- 65 75 parts of methanol
- 90 parts of vinyl acetate
- 10 parts of polyethylene glycol (mol. weight 1,000,000)
- 3.5 parts of diacetyl peroxide in dimethyl phthalate (of about 28% strength).

The mixture is boiled for 5 hours under reflux and while stirring. After cooling the reaction product is precipitated in water, suction-filtered, washed well with water and dried at 40°C under reduced pressure. By reprecipitating the polymer from methanolic solution with water the graft polymer can be further purified.

The graft copolymer obtained has a K value of 42 and contains 9% by weight of bound oxethyl groups.

EXAMPLE 9

A graft copolymer is produced as described in Example 2 from

- 85 175 parts of vinyl acetate
- 25 parts of polyethylene glycol (mol. weight about 30,000) reacted at the terminal hydroxyl groups with p-phenylene-diisocyanate
- 2 parts of dibenzoyl peroxide

The product is purified by dissolution in methanol and precipitation in water. After drying at 40°C under reduced pressure 192 parts of a graft copolymer are obtained having an acetyl content of 42% (pure polyvinyl acetate 50% and containing 15.4% of bound oxyethyl groups).

EXAMPLE 10

A graft copolymer is prepared as described in Example 1 from

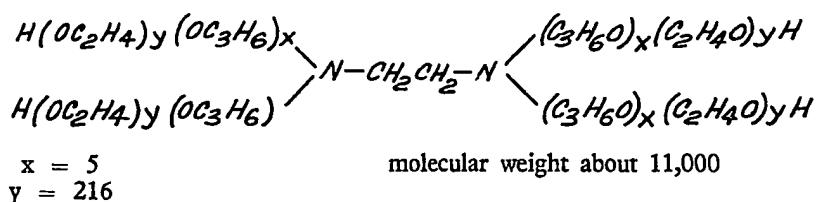
- 100 90 parts of vinyl acetate
- 90 parts of vinyl propionate
- 20 parts of polyethylene glycol (molecular weight 4,000)
- 2 parts of dibenzoyl peroxide

The graft copolymer purified by reprecipitation from a methanolic solution with water contains 6% by weight of bound oxyethyl groups.

EXAMPLE 11

In a suitable wide-necked glass bottle provided with reflux condenser and dropping funnel there are heated in a water bath of 80°C, until polymerization sets in, 5 parts of a solution of

- 110 89% by weight of vinyl acetate
- 1% by weight of dibenzoyl peroxide
- 10% by weight of nitrogen-containing oxyethylated polypropylene glycol of the following constitution



5 The polymerization having started, further 95 parts of the above solution are added in the course of about 2 hours whereby the reaction mixture is heated to the boil. The addition of monomer being terminated, the temperature of the bath is raised to 90°C and maintained at said temperature for 2 hours to complete the polymerization. Finally the unreacted 10 monomer is removed under a pulsating vacuum.

15 After cooling, the glass bottle with the polymer is frozen in dry ice, the bottle is smashed and the polymer is isolated. 95 parts of a clear yellowish graft copolymer are obtained which is purified by dissolution in

acetone and reprecipitation in water. The product is dried in a vacuum drier at 40°C until the weight remains constant. The product has a K value of 4.5 (according to Fikentscher, "Cellulosechemie," volume 13, page 58, 1932; 1% in ethyl acetate) and a relative viscosity of 1.55 (1% in ethyl acetate). A polyvinyl acetate prepared under identical conditions but in the absence of the nitrogen-containing oxyethylated polypropylene glycol has a K value of 55—60.

The product which has three times been reprecipitated has the following analytical data:

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Composition	Graft copolymer	Comparative polyvinyl acetate
% of carbon	54.7	56.2
% of hydrogen	7.0	7.0
% of acetyl	45.5	50.0
% of oxyethyl (Morgan)	7.6	—

35 When a film is made from this product it is flexible, in contradistinction to a film of pure polyvinyl acetate having the same molecular weight.

EXAMPLE 12

40 A four-necked flask with ground stopper (capacity 1 liter) provided with stirrer, dropping funnel, reflux condenser and thermometer is charged with the following solution:

45 250 parts of methyl acetate
195 parts of vinyl acetate
50 parts of a nitrogen-containing oxyethylated polypropylene glycol as defined in Example 17

50 5 parts of diacetyl peroxide in dimethyl phthalate (of about 30% strength).

55 The mixture is boiled for four hours under reflux. After said reaction period the solid content amounts to 49.7%. The whole is then allowed to cool and the polymer is precipitated in water. The product is dissolved repeatedly in methyl acetate and reprecipitated in water.

55 The purified copolymer is then dried at 40°C in a vacuum drier. There are obtained 220 parts of a clear yellowish resin. The copolymer has an acetyl value of 39.5% as compared

with 50% for pure polyvinyl acetate. The K value is 36.5 (1% in ethyl acetate) and the content of ethylene oxide in the polymer amounts to 16%.

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EXAMPLE 13

65 A suitable wide-necked glass bottle provided with dropping funnel and reflux condenser is charged with 10 parts of a solution of

180 parts of acrylic acid methyl ester
20 parts of polyethylene glycol (mol. weight 25,000)
1 part of dibenzoyl peroxide.

The solution is heated on the water bath until polymerization sets in. The rest of the solution is then dropped in in the course of about 2 hours while the mixture boils under reflux at a temperature of the water bath of 80—90°C.

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75 The addition of the monomer being terminated, the boiling ceases and the temperature of the water bath is raised for 2 further hours to 99°C in order to complete the polymerization of the reaction mixture. The unreacted monomer is then removed under a pulsating vacuum.

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85 The copolymer is isolated by freezing the

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bottle in solid ice and subsequently smashing the bottle. The product can be used in this form for many utilitarian purposes.

5 In order to free the graft copolymer from unbound polyethylene glycol, it is dissolved

in methyl acetate and precipitated in water, filtered off and dried at 40°C under reduced pressure. This procedure is repeated thrice. A clear graft polymer is obtained having the following analytical data:

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Graft copolymer	Comparative polymer (without polyethylene glycol residues)
K value (Fikentscher)	56
saponification number	570
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EXAMPLE 14

A solution of
 15 180 parts of acrylic acid methyl ester
 20 parts of polyethylene glycol (mol. weight
 4,000)
 1 part of dibenzoyl peroxide

is polymerized as described in Example 13.

The copolymer obtained is purified by dissolving it in methyl acetate and reprecipitating it thrice in water. It has the following analytical data:

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Graft copolymer	Comparative polymer (without polyethylene glycol residues)
K value (Fikentscher)	41
saponification number	595
	640

25 Specification No. 874,130 claims a co-polymer of vinyl acetate and a polyoxyalkylene compound, as defined in the Specification, and a process for making such copolymers, which comprises making a mixture consisting of vinyl acetate and a polyoxyalkylene com-

free radical polymerisation catalyst and/or under the action of actinic light.

30 3. A process as claimed in claim 1 or claim 2, wherein the polyalkylene oxide or polyalkylene glycol is dissolved in the monomer or monomers in the presence of an additional solvent.

35 4. A process as claimed in any one of claims 1 to 3, wherein the free radical catalyst is an organic peroxide.

40 5. A process as claimed in claim 4, wherein the free radical catalyst is diacetyl peroxide, dibenzoyl peroxide, dilauroyl peroxide or α -azodiisobutyronitrile.

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45 6. A process as claimed in any one of claims 1 to 5, wherein the solution to be polymerised also contains a co-polymerizable monomer selected from the group consisting of crotonic acid, acrylic acid, methacrylic acid, maleic acid esters, fumaric acid esters and itaconic acid esters.

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50 7. A process as claimed in any one of claims 1 to 6, wherein a redox system is used as the free radical catalyst.

55 8. A process as claimed in claim 7, wherein dibenzoyl-peroxide and benzoin is used as the redox system.

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55 9. A process as claimed in any one of claims 1 to 8, wherein the free radical catalyst is present in an amount ranging from 0.01 to 10 per cent, calculated on the weight of the monomer or monomers.

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10. A process as claimed in any one of claims 1 to 9, wherein the polymerisation is carried out at a temperature ranging from 50 to 100°C. 55
- 5 11. A process as claimed in any one of claims 1 to 10, wherein the polyalkylene glycol is polyethylene glycol having a molecular weight within the range of 106 to several millions.
- 10 12. A process as claimed in claim 11, wherein a polyethylene glycol having a molecular weight within the range of 1,000 to 30,000 is used. 60
- 15 13. A process as claimed in any one of claims 1 to 12, wherein vinyl acetate is used as the vinyl ester monomer. 65
14. A process as claimed in any one of claims 1 to 13, wherein the polyalkylene oxide is a copolymer of ethylene oxide with at least one member selected from the group consisting of propylene oxide, 1:2-epoxy-butane, isobutylene oxide and styrene oxide.
- 20 15. A process as claimed in any one of claims 1—13, wherein a polyalkylene glycol with etherified terminal hydroxyl groups is used. 70
- 25 16. A process as claimed in any one of claims 1—13, wherein a polyalkylene glycol with esterified terminal hydroxyl groups is used. 75
- 30 17. A process as claimed in any one of claims 1 to 13, wherein the polyalkylene glycol is an oxyethylated polypropylene glycol consisting of a central portion of polypropylene glycol having a molecular weight of 2,000 to 12,000 which central portion has been reacted at both sides with from 40 to 70 mols of ethylene oxide.
- 35 18. A process as claimed in any one of claims 1 to 13, wherein the polyalkylene glycol is a compound of the general formula 80
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- $$\begin{array}{c} \text{HOR} \\ | \\ \text{N}-\text{R}_1-\text{N} \\ | \\ \text{HOR} \end{array}, \quad \begin{array}{c} \text{ROH} \\ | \\ \text{N}-\text{R}_1-\text{N} \\ | \\ \text{ROH} \end{array},$$
- 45 wherein R stands for an alkylene oxide chain with 3 to 2,000 alkylene oxide units and R₁ represents a hydrocarbon radical. 85
19. A process as claimed in any one of claims 1 to 13 wherein the polyalkylene glycol is a compound of the general formula 90
- $$\begin{array}{c} \text{ROH} \\ | \\ \text{R}_2\text{N} \\ | \\ \text{ROH} \end{array}$$
- 50 wherein R represents an alkylene oxide chain with 3 to 2,000 alkylene oxide units and R₂ represents a carboxylic or organic sulphonic acid radical. 95

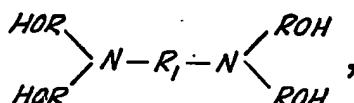
represents a carboxylic or organic sulphonic acid radical.

20. A process for the manufacture of a graft copolymer conducted substantially as described in any one of the Examples herein.

21. A graft copolymer comprising a polyalkylene oxide or polyalkylene glycol, as trunk polymer, containing chains of one or more polymers in graft relationship thereto.

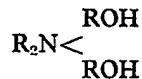
22. A graft copolymer comprising a polyalkylene oxide or polyalkylene glycol, as trunk polymer, containing chains of one or more polyvinyl esters, polyacrylic acid esters or polymethacrylic acid esters in graft relationship thereto.

23. A graft copolymer comprising a compound of the general formula



wherein R stands for an alkylene oxide chain with 3 to 2,000 alkylene oxide units and R₁ represents a hydrocarbon radical, containing chains of one or more polyvinyl esters, polyacrylic acid esters or polymethacrylic acid esters in graft relationship thereto.

24. A graft copolymer which comprises a compound of the general formula



wherein R represents an alkylene oxide chain with 3 to 2,000 alkylene oxide units and R₂ represents a carboxylic or organic sulphonic acid radical, containing chains of one or more polyvinyl esters, polyacrylic acid esters or polymethacrylic acid esters in graft relationship thereto.

25. A graft copolymer which comprises a polyalkylene glycol containing in graft relationship thereto chains of a copolymer of a vinyl ester, acrylic acid ester or methacrylic acid ester with crotonic acid, acrylic acid, methacrylic acid, a maleic acid ester, a fumaric acid ester or an itaconic acid ester.

26. A graft copolymer when obtained by the process claimed in any one of claims 1 to 20.

27. A graft copolymer as claimed in claim 21 and substantially as described in any one of Examples 1—3, 5, 7 and 9—14 herein.

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